ON THE

DERIVATIVES OF MESITYLEN.

INAUGURAL-DISSERTATION

FOR THE

DEGREE OF DOCTOR OF PHILOSOPHY

AT THE

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1867.

The following researches were undertaken at the suggestion of Professor Fittig, to whom and my most respected teacher Professor Wöhler, I would offer my most sincere thanks for the many attentions given to me while studying in the laboratory.

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By the destructive distillation of metallic acetates in an anhydrous state, there is obtained among other products, acetone, or pyroacetic spirit.

Sir Robert Kane [1]) in his researches on this substance discovered that by the action of sulphuric acid a liquid hydrocarbon was formed which he described under the name of mesitylen.

It is this hydrocarbon which is the subject of the following researches, and I think it will not be without interest to give here a short sketch of its history.

Kane considered acetone as the hydrated oxide of a compound radical mesityl, analogous to methyl, ethyl &c.

$$HO, C_6H_5O.$$

Mesitylen he regarded as the olefiant gas of his new series. His opinion appeared to be confirmed by the analysis, which gave results leading to the formula C_3H_2, but both the production of this body as being derived from acetone, and the products into which it was converted by various agents proved that the equivalent was higher. In fact the preparation of a crystalline body by the action of chlorine on mesitylen and described by Kane under the name of chloride of pteleyl obliged him to double the formula into the following expressions

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[1]) Journal für Chemie, vol. 15, p. 129.

Mesitylen C_6H_4,

Chloride of Pteleyl C_6H_3Cl,

a change which rendered the transformation of acetone perfectly analagous to that of alcohol under the same circumstances.

$$\underset{\text{Alcohol.}}{C_4H_6O_2} - 2HO = \underset{\text{Olefiant gas.}}{C_4H_4}$$

$$\underset{\text{Acetone.}}{C_6H_6O_2} - 2HO = \underset{\text{Mesitylen.}}{C_6H_4}$$

This formula for mesitylen appeared to be confirmed by the composition of the corresponding Bromine and Nitro compounds

$$C_6H_3Br, C_6H_3NO_4$$

which at a later period were discovered by Cahours [1]) who in hopes of obtaining further support to this formula determined the vapour density of mesitylen. The result of this determination led many to double the formula of mesitylen into $C_{12}H_8$.

The only thing which did not well agree with this formula was the boiling point which for a hydrocarbon of the Composition $C_{12}H_8$, was very high. Gmelin in his handbook mentioned this, and remarked that the boiling point agreed better with a compound of the formula $C_{18}H_{12}$.

Hofmann [2]) was the first to show that this was the proper formula for mesitylen. By the action of Nitric acid he obtained a body which on analysis gave the formula $C_9H_5NO_4$; this did not agree with the formula already assigned to it, so it was found necessary to double the formula into $C_{18}H_{10}(NO_4)_2$, which was con-

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[1]) Annalen der Chemie, vol. 64, p. 396.

[2]) do. vol. 71, p. 121.

firmed by the formula of nitro-mesidine prepared by Maule [1]).

In his memoir Hofmann speaks of the vapour density estimation as very probably being wrong. This led Cahours to make a new estimation, when he found results also agreeing with the formula $C_{18}H_{12}$, mentioning as the cause of the first estimation giving such low results, that he took the substance boiling at 135.5° C. as given by Kane, whereas in his second estimation Cahours [2]) found that the boiling point lay much higher.

This hydrocarbon is interesting on account of its being one of the very few cases in which the change from the one great group of organic compounds to the other, is capable of being followed and explained by means of formulae, the change taking place simply by the abstraction of the constituents of water

$$3(C_3H_6O) - 3H_2O = C_9H_{12}.$$

For a long time it was overlooked, and not regarded as belonging to the group of Aromatic Compounds, until Fittig [3]) shewed that it was entitled to a place in that group with as much right as Toluol and Xylol.

By means of oxydation it is changed into an acid having the same relation to mesitylen that Benzoic acid has to Toluol

$$\underset{\text{Toluol.}}{C_7H_8} + 3O = \underset{\text{Benzoic acid.}}{C_7H_6O_2} + H_2O$$

$$\underset{\text{Mesitylen.}}{C_9H_{12}} + 3O = \underset{\text{Mesitylenic acid.}}{C_9H_{10}O_2} + H_2O$$

The Bromine and Nitro compounds are in every

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1) Annalen der Chemie, vol. 71, p. 137.

2) do. vol. 74, p. 106.

3) do. vol. 141, p. 130.

respect similar to those obtained from the group of Aromatic Compounds, and it was with the intention of filling up the gaps by completing the series of the Nitro and Bromine compounds that the following investigations were undertaken.

Preparation of Mesitylen.

The hydrocarbon used in the following experiments was prepared by the process recommended by Kane [1]), viz., by distilling two volumes of anhydrous acetone with one volume of concentrated sulphuric acid.

It is advisable to put a small quantity of dry sand into the retort, as that effectually prevents the mixture from foaming up and passing into the receiver. On the addition of the sulphuric acid to the acetone the action is so energetic that distillation begins without the application of heat, the contents of the retort soon become of a beautiful blue color, which, as the distillation proceeds, gradually deepens in intensity until it is finally replaced by black, from the separated carbon.

During the whole process streams of sulphurous acid and other gases are evolved, among which, judging by the smell, Fittig [2]) mentions allylene.

The crude distillate consists of an aqueous solution of sulphurous acid and acetone, on the surface of which floats a greenish yellow oil. This is the impure mesitylen. It is first freed from the sulphurous acid and acetone by repeated washing with water, dried over chloride of calcium and then subjected to fractional distillation.

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1) Journal für Chemie Vol. 15. p. 131.

2) Annalen Vol. 141. p. 131.

The liquid begins to boil below 100° and rises gradually till above 200°; in fact fully one half of the crude mesitylen has a boiling point above that temperature. Only after long continued fractional distillation, for the last three or four times over sodium, is it possible to obtain the hydrocarbon in a state of purity. As the crude mesitylen always contains acetone and other bodies containing oxygen, Fittig [1]) hoped to obtain a better yield by increasing the quantity of sulphuric acid; contrary to expectation a smaller yield was obtained, a larger quantity of carbon than usual remaining in the retort. By allowing the mixture of acetone and sulphuric acid to stand for about twelve hours and then slowly distilling a larger yield is obtained than by distilling as soon as the substances are mixed.

Under the most favourable circumstances the yield of pure mesytilen is very small in comparison to the quantity of acetone used, about 15 per cent. being the average yield.

The boiling point of mesitylen as found by Fittig [2]) is 163°, this agrees pretty closely with that given by Cahours [3]) (162 — 164°), while that of Hofmann [4]) (155—160°) is rather low, Kane's [5]) estimation (135. 5°) being much too low.

When pure, mesitylen is a colorless limpid fluid, of a peculiar but not at all disagreeable smell. Kane speaks of it as possessing an odour resembling garlic, which he mentioned as very characteristic of this hydrocarbon. This is true of the crude mesitylen, but by

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1) Annalen, vol. 141. p. 132.
2) Annalen, vol. 141. p. 132.
3) Annalen, vol. 74. p. 107.
4) Annalen, vol. 71. p. 121.
5) Journal für Chemie, vol. 15. p. 129.

distillation over sodium, the odour is completely removed. It is possible that it is owing to the presence, in small quantity, of a sulphur compound.

Nitro-Mesitylen.

In the cold, ordinary nitric acid of Sp. Gr. 1.38 has little or no action on mesitylen and only on heating in a water bath does union take place. Once begun the action is very energetic and proceeds without the aid of further heat.

The result, after all action has ceased when poured into water yields a dark brown oil which sinks beneath the surface. After washing free from acid and distilling with water it yields a yellowish oil which passes over with the steam and condenses in the receiver, a quantity of a brown resinous looking substance remaining in the retort.

Several attempts were made to obtain crystals from this oil by dissolving in alcohol, and allowing to evaporate spontaneously, however without success, the oil even when cooled with a mixture of ice and common salt still retained its liquid form. Finally the oil was distilled; at first a quantity of unchanged mesitylen passes over, then the mercury rises rapidly till it reaches a temperature of about 220°, between this and 250° the greater part distills off, above 250° the oil begins to decompose, and finally becomes converted into a mass of carbon.

The distillate between 220° and 250° when cooled solidifies for the most part to a crystalline mass, what still remains liquid is drained off, the crystals dissolved in alcohol, and purified by recrystallization.

Nitro-mesitylen is very soluble in boiling alcohol, from which, on cooling it is deposited in long prisms very slightly tinged with yellow, having their melting point at 41°, and at a temperature between 230 and 240° capable of being distilled without decomposition. When analysed the following results were obtained.

0,1975 grm. substance gave
0,4725 „ carbonic acid, and
0,12325 „ water.

		Theory	Analysis
C_9	108	65,455	65,265
H_{11}	11	6,670	6,931
NO_2	46	27,875	—
	165	100.	

The above numbers agree therefore very closely with the formula $C_9H_{11}NO_2$.

By treating mesitylen with nitric acid Cahours [1]) found that a dark yellow oil was produced, which he regarded as nitro-mesitylen. Hofmann [2]) when preparing dinitro-mesitylen also obtained this oil but not in sufficient quantity for analysis. Cahours observes further, that by the action of an alcoholic solution of potash, the oil was decomposed and yielded a compound which crystallized from alcohol in beautiful tabular crystals. As a rule nitro-mesitylen crystallizes in long prisms; on one occasion it was obtained in the above mentioned form, several of the crystals being about an inch in length and nearly half an inch in breadth.

It is very possible that this was the pure nitro-mesitylen, and that only impurities were decomposed and removed by the potash.

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[1]) Compt. rend.

[2]) Annalen, vol. 71. p. 121.

Dinitro-mesitylen

$$C_9H_{10}(NO_2)_2$$

was first prepared by Hofmann [1]), and later, by Fittig [2]) who obtained it by the following process. The mesitylen is gradually dropped into well cooled fuming nitric acid; after allowing the mixture to stand for a short time it is poured into water, the white precipitate thus obtained is washed free from acid and dissolved in alcohol, one recrystallization being all that is necessary to obtain this compound chemically pure.

The dinitro-mesitylen melts at 86°.

It is easily soluble in boiling alcohol from which it crystallizes out on cooling in long colorless shining needles.

The great ease with which mesitylen is changed into this crystalline compound is so characteristic that Fittig suggested is as the best means of recognizing this hydrocarbon.

Trinitro-mesitylen.

$$C_9H_9(NO_2)_3.$$

This was the first known nitro derivative of mesitylen, and we are indebted for its discovery to Cahours [3]).

By the action of a mixture of nitric and sulphuric acids he obtained a crystalline compound, which, when

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1) Annalen, vol. 71. p. 121.
2) do., vol. 141. p. 132.
3) do., vol. 64. p. 396.

purified by washing with water, and repeated crystallizations from alcohol, exhibited the lustre of metallic silver in a remarkable degree.

In boiling alcohol it is not very soluble, a better solvent is acetone, from which it crystallizes in large, transparent, colorless prisms. The melting point of the crystals as observed by Fittig lies between 230° and 232°.

Mesitylenamin.

$C_9H_{11}(NH_2)$.

This base was prepared by heating a quantity of the nitro-mesitylen crystals with granulated tin and hydrochloric acid, long continued boiling being necessary for their complete reduction. After all action had ceased, the solution was diluted with water, filtered, and the tin in the solution precipitated by means of Sulphuretted hydrogen, the base remaining dissolved as hydrochloric acid salt. The solution was now evaporated, towards the end of the operation, conducting the process in a water bath, heating till all excess of hydrochloric acid was expelled.

On dissolving the residue in water, and adding caustic ammonia to the solution the free base was obtained as a colorless oil [1]), which, in the form of small drops, was diffused through the liquid, it being apparently of about the same specific gravity as water.

The preparation of the oil in quantity sufficient for analysis being attended with many difficulties, an analysis

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[1]) Not solid, as described in the „Zeitschrift für Chemie". 1867. p. 104.

of the salt it forms with oxalic acid was made for the purpose of determining its composition, (for analysis see page 16). The oil diffused through water when cooled to a temperature of 0° retains its liquid form.

Salts of Mesitylenamin.

Double Salt $(C_9H_{11}(NH_2),HCl)_2+SnCl_2$.

The concentrated solution obtained by the reduction of nitro-mesitylen with tin and hydrochloric acid, deposits on cooling small needleformed crystals of this salt. By using crystals of nitro-mesitylen, the salt so obtained is chemically pure, and it is only necessary to separate the crystals by filtration and dry over sulphuric acid when the salt is in a condition fit for analysis.

For the estimation of the tin, the crystals were treated with nitric acid, ignited to drive off the organic matter, residue moistened with nitric acid, again heated, and the tin weighed as SnO_2.

Analysed as above,

0,327 grm. substance gave
0,0905 grm. SnO_2.

		Theory	Analysis
C_{18}	216	40,602	—
H_{28}	28	5,263	—
Cl_4	142	26,692	—
N_2	28	5,263	—
Sn	118	22,180	21,688
	532	100.	

In water the crystals are dissolved with partial decomposition, oxide of tin being precipitated; a small quantity of hydrochloric acid added to the water prevents this change from taking place.

Hydrochloric acid salt.

$C_9 H_{11} NH_2 HCl$.

The solution of the double salt $(C_9 H_{11} NH_2, HCl)_2 + Sn Cl_2$ in hydrochloric acid, after precipitation of the tin by means of sulphuretted hydrogen, yields on evaporation fine feathery crystals of the above mentioned salt. The crystals when pure are quite colorless, are very soluble in water and also in alcohol.

Analysis gave following results

0,163 grm. substance gave
0,1339 grm. Chloride of Silver.

		Theory	Analysis
C_9	108	62,973	—
H_{14}	14	8,164	—
N	14	8,164	—
Cl	35,5	20,699	20,318
	171,5	100.	

Oxalic acid salt.

$(C_9 H_{11} NH_2)_2 H_2 C_2 O_4$.

On adding ammonia to the hydrochlorate of mesitylenamin, the free base is obtained in the form of an oil; an alcoholic solution of this oil, when added to a solution of oxalic acid, yields a crystalline precipitate which is in cold water difficultly soluble. A quantity of the salt so obtained, after separation of the excess of oxalic acid by washing with water, was subjected to analysis and the oxalic acid estimated by precipitation with chloride of calcium; result showed that the salt was a mixture of acid and neutral oxalate of mesitylenamin.

To obtain the neutral salt it was therefore found necessary to add a solution of neutral oxalate of ammonia to the hydrochlorate of mesitylenamin, when the neutral salt was precipitated in white shining crystalline plates. After washing with water, to free it from chloride of ammonium, the salt was dissolved in boiling water, evaporated to a small bulk, and allowed to crystallize. The solution yielded no crystals, and on evaporating to dryness in the water bath, a quantity of an amorphous substance was obtained, whose appearance differed entirely from the original salt.

On redissolving in water and adding ammonia to the solution, the free base was not precipitated, thus showing that the salt had, during the evaporation, undergone a very remarkable decomposition. The precipitate of the neutral salt after washing with cold water, was dried over sulphuric acid and analysed with the following results

0,131 grm. substance gave
0,3169 grm. Carbonic acid and
0,095 grm. Water.

		Theory	Analysis
C_{20}	240	66,666	65,95
H_{28}	28	7,778	8,01
N_2	28	7,778	—
O_4	64	17,778	—
	360	100.	

Nitromesitylenamin.

$C_9H_{10}(NO_2)NH_2$.

This compound was prepared and described by

Maule [1], who obtained it by submitting an alcoholic solution of dinitromesitylen to the action of sulphuretted hydrogen so long as that reagent was absorbed. On addition of hydrochloric acid to the saturated solution, sulphur was precipitated, this was separated by filtration, when a clear liquid was obtained, which on being mixed with ammonia gave a copious precipitate.

By repeated dissolving in hydrochloric acid and reprecipitation with alkali, the last traces of sulphur were removed and the nitromesitylenamin obtained of a bright yellow color. It is very soluble in alcohol from which it crystallizes in long needle shaped crystals of a golden yellow color, having their melting point below 100°. In water it is slightly soluble, imparting to the solution a faint yellow color.

Mesitylendiamin.

$C_9H_{10}(NH_2)_2$.

By treating the dinitromesitylen with tin and hydrochloric acid in the same manner as nitromesitylen, Fittig [2] obtained the above mentioned base. The details of the process, and the properties of this compound as described by him, are as follows.

After separation of the tin by means of sulphuretted hydrogen, the solution gave on evaporation the hydrochloric acid salt. When ammonia is added to a concentrated hot solution of this salt, the free base is precipitated as a nearly colorless oil, which on cooling becomes solid. A few crystallizations from hot water

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1) Annalen vol. 71, 137.

2) Annalen vol. 141, p. 134.

render the base pure. In boiling water it is rather soluble, not so much so in cold; in alcohol and ether it is very soluble.

Crystallized from water it is obtained in long hair like colorless needles, from ether in large transparent monoclinic prisms. By keeping, especially in the light, the base becomes yellow or red, owing probably to oxidation. The crystals melt at 90°, and by careful heating sublime in shining needles.

Dinitromesitylenamin.

$$C_9 H_9 (NO_2)_2 NH_2.$$

This compound was discovered and described by Fittig [1]), who obtained it by treating Trinitromesitylen with sulphuretted hydrogen.

The following are the properties of this base. In water it is nearly insoluble, in alcohol easily soluble, from which it crystallizes in yellow prisms having their melting point between 193—194°.

Its basic properties are very weak, and it is nearly as insoluble in dilute acids as in water. When heated with concentrated hydrochloric acid it is dissolved, the solution depositing on cooling small colorless crystals. This is the hydrochloric acid salt, but it is so unstable that when brought into contact with water it is immediately decomposed.

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[1]) Annalen vol. 141, p. 138.

Nitromesitylendiamin.

$C_9 H_9 (NO_2) (NH_2)_2$.

When trinitromesitylen is subjected to the long continued action of sulphuretted hydrogen in presence of ammonia, it is slowly converted into the above mentioned base.

Its properties were described by Fittig [1]), and are as follows.

It is nearly insoluble in cold and difficultly in hot water, in alcohol and ether it is easily soluble. The crystals obtained from the hot water solution are orange colored plates. By the spontaneous evaporation of its alcoholic solution it crystallizes out in well formed crystals of great brilliancy, and possessing a color very much resembling that of the nitroprusside of sodium. Its melting point is 184°, and it combines readily with acids, forming salts with them.

1) Annalen vol. 141, p. 139.

Bromine derivatives of mesitylen.

Brommesitylen.

$C_9 H_{11} Br$.

Bromine has a very energetic action on mesitylen, and it was found necessary for the preparation of this compound to use the Bromine and mesitylen in equivalent proportions.

One molecule Bromine was added by means of a fine capillary tube to one equivalent mesitylen at the same time keeping the hydrocarbon well cooled with water, this however did not prevent the formation of a small quantity of di- and tribrommesitylen, free mesitylen being also found in the liquid.

The mesitylen retained its liquid form and at the end of the operation the oil was washed, first with alkali to neutralize the hydrobromic acid, then with water to separate the alkali. After drying over chloride of calcium it was subjected to fractional distillation, when after numerous distillations, a colorless oil possessing a slightly aromatic odour passed over at a temperature of 225°.

During the first two or three distillations a brilliant red coloring matter passed over and was deposited on the sides of the receivers. This coloring matter, which

had a great resemblance to those produced from analine, was almost instantaneously decomposed by water, the resulting solution having a slightly brown tinge. In alcohol it is also freely soluble with however partial loss of its brightness, which can be again restored by heating with hydrochloric acid. The alcoholic solution on remaining exposed to the air for several days was also decomposed, a small quantity of brown sediment alone remaining. The quantity at my disposal was so very minute that I found it impossible to determine its exact nature.

For the estimation of the bromine a quantity was heated in a narrow combustion tube with pure dry caustic lime, the result was dissolved in nitric acid, filtered to separate from carbon, and the bromine precipitated with nitrate of silver.

Treated as above
,1755 grm. substance gave
,1649 grm. Bromide of Silver.

		Theory	Analysis
C_9	108	54,272	—
H_{11}	11	5,527	—
Br	80	40,201	39,983
	199	100.	

At a temperature of 10° it has a specific gravity of 1,3191. When cooled with a mixture of ice and common salt to a temperature of —11° it is converted into a mass of white needle shaped crystals. A thermometer inserted into the crystals when melting showed the temperature of —1°.

Dibrommesitylen.

$C_9H_{10}Br_2$.

The residue remaining in the retort after the distillation of the monobrommesitylen becomes solid on cooling. By heating with alcohol, filtering to separate from carbon and allowing solution to crystallize, crystals are deposited. These are a mixture of di- and tribrom compounds and several recrystallizations are necessary to obtain the dibrommesitylen in a state of purity. It can also be prepared in larger quantity by the same method as is used for the preparation of monobrommesitylen, using two molecules bromine instead of one, and conducting the process with all the precautions as detailed in page 20.

After several hours the hydrocarbon becomes solid. It is then washed, first with alkali, and afterwards with water, dried by pressing between folds of filtering paper, dissolved in alcohol and allowed to crystallize; two or at most three recrystallizations being all that is necessary to obtain this derivative pure.

It crystallizes in long fine white needles, sometimes fully an inch in length, having their melting point at 60 and distilling at a temperature of 285° without decomposition. The crystals are freely soluble in alcohol.

When analysed

,18575 grm. substance gave

,2522 grm. Bromide of Silver.

		Theory	Analysis
C_9	108	38,849	—
H_{10}	10	3,596	—
Br_2	160	57,555	57,765
	278	100.	

Tribrommesitylen.

$C_9H_9Br_3$.

This derivative of mesitylen was prepared first by Cahours, and afterwards by Hofmann. It is prepared by treating one equivalent mesitylen with three molecules bromine.

It crystallizes from alcohol in white needles which are volatile without decomposition. In cold alcohol it is with difficulty soluble and also in ether. Its best solvent is benzole from which it is deposited by spontaneous evaporation in small well formed monoclinic prisms. The melting point of the crystals is 224°.

Action of concentrated nitric acid on brommesitylen.

A mixture consisting of equal volumes of fuming and ordinary concentrated nitric acid acts very gradually on brom mesitylen, and only after being in contact with the acid for several hours does the oil become solid.

It is then washed with water to free it from acid, dried between folds of filtering paper, and heated with alcohol in which it readily dissolves. On cooling hair-like needles of dinitrobrommesitylen are deposited. The mother liquor on further evaporation yields crystals which are a mixture of mono- and dinitrobrommesitylen. After numerous recrystallizations the

Mononitrobrommesitylen

$C_9H_{10}BrNO_2$

is obtained in crystals very much resembling those of chloride of ammonium. The crystals are very nearly

colorless, and dissolve freely in boiling as well as in cold alcohol. Their melting point is 54°.

Analysis was made with the following results.

I. ,19375 grm. substance gave
,3128 „ Carbonic Acid and
,076 „ Water.

II. ,12275 „ substance gave
,0952 „ Bromide of Silver.

		Theory	Analysis	
			I.	II.
C_9	108	44,262	44,031	—
H_{10}	10	4,098	4,356	—
Br	80	32,788	—	33,002
NO_2	46	18,852	—	—
	244	100.		

The action of fuming nitric acid on brommesitylen is more energetic, and converts that derivative in a short space of time into a whitish looking solid; this when washed with water, dried, and dissolved in alcohol yields crystals of the

Dinitrobrommesitylen

$C_9H_9Br(NO_2)_2$.

In cold alcohol it is sparingly soluble, but more freely in boiling alcohol from which on cooling it crystallizes in small needles, melting between 189 and 190°. The crystals when slightly heated evolve an odour resembling that of musk.

An ultimate and a bromine analysis gave the following results.

I. 0,18965 grm. substance gave
0,25825 „ Carbonic Acid and
0,05625 „ Water.

II. 0,181 „ substance gave
0,11675 „ Bromide of Silver.

		Theory	Analysis	
			I.	II.
C_9	108	37,370	37,137	—
H_9	9	3,114	3,299	—
Br	80	27,682	—	27,442
$(NO_2)_2$	92	31,834	—	—
	289	100.		

Brommesitylenic acid

$C_9H_9BrO_2$.

Monobrommesitylen when boiled for two days with ordinary concentrated nitric acid diluted with twice its volume of water, is converted for the most part into a crystalline substance almost insoluble in water.

The mixture is allowed to cool and the acid and brommesitylen separated from the water by means of filtration. The insoluble part is heated with a slight excess of carbonate of sodium, which dissolves out the acid, and leaves the still unchanged brommesitylen behind. On the addition of hydrochloric acid to the soda solution the brommesitylenic acid is obtained as a white flocculent precipitate. This is collected, washed with water, dried between folds of filtering paper and then dissolved in alcohol from which it crystallizes out in small clear compact prisms.

So obtained the acid is always contaminated with minute quantities of Nitrobrommesitylenic acid, which is also formed during the heating with nitric acid. The most convenient method of obtaining the acid pure, is by using chromic acid as oxidizing agent. The yield is not so large, but it has the advantage of giving an acid free from the nitrobrommesitylenic acid.

It is prepared by heating brommesitylen for one day with bichromate of potassium, sulphuric acid and water, at the end of that time a further quantity of water is added and all unchanged brommesitylen distilled over with the water vapours.

The mixture is then allowed to cool, the acid filtered off and washed with water. The further details of the process are the same as those used in the preparation of the acid obtained by oxidation with Nitric acid.

If the oxidation is carried on further, and the brommesitylen heated for two days, the yield of acid is much diminished owing to its being further oxidized and converted into acetic acid. Its melting point is 212°, and at a temperature a little above that it partially sublimes, condensing in long fine colorless needles. Subjected to analysis the following results were obtained.

I.	0,18425	grm.	Acid gave
	0,316	„	Carbonic Acid and
	0,066	„	Water
II.	0,1518	„	Acid gave
	0,1255	„	Bromide of Silver.

		Theory	Analysis	
			I.	II.
C_9	108	47,161	46,774	—
H_9	9	3,930	3,978	
Br	80	34,935	—	35,180
O_2	32	13,974	—	—
	229	100		

The acid is easily soluble in alcohol, and almost insoluble in water.

Salts of Brommesitylenic acid.

Barium salt

$Ba(C_9H_8BrO_2)_2$,

was obtained by heating a quantity of the acid with carbonate of barium until the solution was neutral to testpapers. The excess of carbonate of barium is separated by filtration and the filtrate evaporated. On cooling, the above salt crystallized out in fine needle shaped white crystals. These were carefully collected, dried by pressing between folds of filtering paper and finally allowed to remain over sulphuric acid for several days.

When analysed

0,21125 grm. Salt gave
,083 „ Sulphate of Barium.

		Theory	Analysis
$2(C_9H_8BrO_2)$	456	76,897	—
Ba	137	23,103	23,105
	593	100.	

The salt dried over sulphuric acid has no water of crystallization. It is easily soluble in boiling water, more difficultly in cold.

Kalium salt.

$K C_9 H_8 Br O_2$.

This salt is best prepared by adding a solution of sulphate of potassium, to the barium salt dissolved in water, taking care to add as little excess of sulphate of potassium as possible. The solution on being separated from the sulphate of barium is evaporated to dryness in a water bath, and the kalium salt dissolved out by means of absolute alcohol which dissolves it freely. This ensures its complete separation from sulphate of potassium. The alcoholic solution after evaporation yields crystals of the salt. For the estimation of the kalium a portion of the salt was heated to redness, residue was then moistened with concentrated sulphuric acid, evaporated completely to dryness and weighed.

Thus treated

0,1035 grm. Salt gave

,03425 „ Sulphate of Potassium.

		Theory	Analysis
$C_9 H_8 Br O_2$	228	85,393	—
K	39	14,607	14,831
	267	100.	

Calcium salt.

$Ca (C_9 H_8 Br O_2)_2$.

On boiling the brommesitylenic acid with finely powdered kalkspar, the above salt is formed. Long continued boiling is necessary before the acid is completely dissolved. A quicker method of preparing the salt is to boil the acid with a slight excess of caustic

lime, filtering and passing carbonic acid through the hot filtered solution, till all free lime is precipitated. By filtering this off and evaporating filtrate the salt crystallizes out in long hair-fine needles. This salt is very soluble in water.

When analysed

0,1445 grm. Salt gave

0,0165 „ CaO.

		Theory	Analysis
$(\mathrm{C_9\,N_8\,Br\,O_2})_2$	456	91,936	—
Ca	40	8,064	8,152
	496	100.	

Action of diluted nitric acid on Nitromesitylen.

A few crystals of nitromesitylen were boiled with nitric acid and water, in the proportions used when oxidizing brommesitylen, for the purpose of seeing if it was possible by this means to obtain Nitromesitylenic acid. After two days boiling the mixture was examined to see if any acid had been formed, it was then found that the nitromesitylen had been carried off by the water vapour and condensed in the Liebig's cooler adapted to the flask, and by that means had escaped oxidation. The crystals were washed into the flask again, and this time the liquid heated, but not to ebullition.

The result was again the same, no acid being formed so that the experiment had to be relinquished.